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Short Communication

One-step, room temperature, colorimetric melamine sensing using an in-situ formation of silver nanoparticles through modified Tollens process

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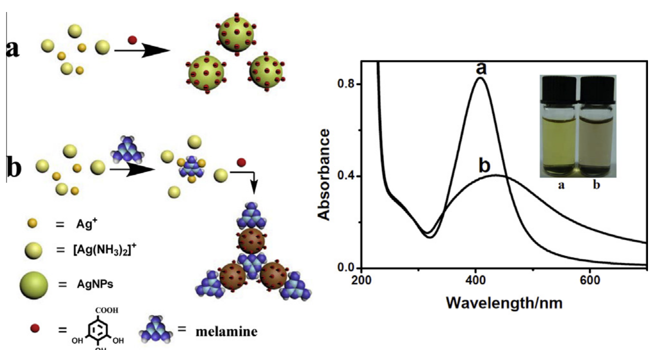
HIGHLIGHTS

- We developed a one-step, RT, and colorimetric method for melamine detection.
- The assay is based on the absorption ratio change of the in-situ formed AgNPs.
- The formed AgNPs are characterized by TEM and UV–vis, respectively.
- The possible mechanism for the aggregation of the formed AgNPs was discussed.
- The method was applied successfully to the determination of melamine in milk samples.

GRAPHICAL ABSTRACT



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ABSTRACT

We have developed a rapid, sensitive, one-step, and selective colorimetric detection method for melamine (MEL) in milk powder based upon an in-situ formation of silver nanoparticles (AgNPs) through modified Tollens process at room temperature. The triazine ring N atoms of MEL molecule were strategically designed to complex the Ag^+ through electron donor–acceptor interaction. During the AgNPs formation procedure, the MEL molecule, which has been covalently bonded with the Ag^+ ions, was adsorbed to the surface of as-prepared AgNPs, resulting in the aggregation of the adjacent AgNPs with detectable decreases of absorption signal. The concentration of MEL can be determined with the naked eye or a UV–vis spectrometer at which the yellow-to-brown color change associated with aggregate enhancement takes place. This method enables rapid (less than 30 min) and sensitive (limit of detection, LOD, 10 nM) detection, and it was also able to discriminate MEL from sixteen other milk relevant coexisting compounds. This assay does not utilize organic cosolvents, enzymatic reactions, light-sensitive dye molecules, lengthy protocols, or sophisticated instrumentation thereby overcoming some of the limitations of conventional methods.

Introduction

Melamine (MEL; 1,3,5-triazine-2,4,6-triamine) is an important organic compound, which is mainly used in producing MEL–formaldehyde resins or as raw material in other chemical industry.

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Due to the high non-protein nitrogen content (66% by mass) of MEL, it is unethically used by milk manufacturers in adulterating milk to make it appear more protein-rich based on the Kjeldahl method for protein analysis in milk products. However, excessive ingestion of MEL can induce renal failure and even death in human beings and animals. A safety limit of MEL has been officially regulated (2.5 ppm in the USA and EU; 1 ppm for infant formula in China) [1]. Consequently, it is important to develop a reliable and highly sensitive method that can detect MEL in milk products on-site and real-time. Up to now, a variety of methods for detecting MEL, such as immunoassay [2–4], GC–MS [5,6], HPLC [7], SERS [8–10], chemiluminescence [11,12], fluorescence [13–16], rayleigh Light Scattering [17,18], surface plasmon resonance [19], capillary electrophoresis [20] and electrochemical method [21] have been reported. Although each of these methods can detect MEL selectively with high sensitivity, most of them are costly, require sophisticated instrumentation and highly trained operators, and time-consuming, which makes rapid and on-site sensing of MEL difficult and limits the scope of their routine applications. On the contrary the colorimetric detection technology for MEL allows detection up to micro/submicromolar levels and that too without involving any expensive instrumentation [22–24]. Therefore, the development of colorimetric sensors for MEL has emerged as a mounting area of significant importance.

In the recent past, coinage metal (Cu, Ag, and Au) nanoparticles-based colorimetric sensors have drawn intense attention. Among them, gold nanoparticles (AuNPs) are the ideal color indicating probes for detection of MEL, which exhibit high extinction coefficients, strongly distance-dependent optical properties, and colors arising from AuNPs at nanomolar concentrations allow them to be easily monitored by the naked eye without the aid of any advanced instruments [25]. In this regard, a number of assays have been developed for MEL based on the label-free or labeled AuNPs [22,26–32]. Lu et al. designed a kind of thiol-functionalized cyanuric acid derivative (MTT)-stabilized AuNPs as a colorimetric sensor for detecting MEL in milk products based on the hydrogen-bonding interaction between MTT and MEL [22]. Additionally, silver nanoparticles (AgNPs) have been paid more attention owing to their plasmon absorbance superior to AuNPs and their easy readout (often with the naked eye) and high sensitivity [33–35].

However, in these strategies, firstly metal nanoparticles are required to be synthesized under demanding reaction conditions, and then they are modified and used for sensing of MEL. The process of metal nanoparticles synthesis and MEL detection are separate, so it needs two or three steps to realize the detection of MEL, which is complicated and make the rapid and on-site detection of MEL in raw milk samples difficult. In this regard, it is necessary to establish a simple, rapid and one-step method for sensing of MEL. Zhao's group explored the formation process of AuNPs as MEL colorimetric probes for the sensitive detection of MEL in real sample [36,37]. However, the low-cost and low-toxic determination has not been realized. Ma et al. recently reported that one-step visual detection of MEL in raw milk during the synthesis process of silver/dopamine nanoparticles [38], but the reaction reagents are expensive such as dopamine. Importantly, the manipulation process was laborious and time-consuming following their use. Furthermore, its signal induction mechanism has not been elucidated clearly.

In this paper, we have designed a new rapid and one-step method for direct determination of MEL through the well-known Ag-mirror reaction. The detection of MEL has been achieved within 30 min at room temperature through monitoring MEL induced aggregation of the forming AgNPs. That is, the MEL determination and the AgNPs formation were realized in one step. As well known, it is a usual phenomenon that nanoparticles adsorb the parent ions on its surface, after the AgNPs forming, the Ag^+ would remain adsorbed on the surface of as-prepared AgNPs. When MEL was added to the abovementioned solution, due to strong electron donor–acceptor interaction of the triazine ring N atoms of MEL with Ag^+, the MEL molecule bonded with the Ag^+ ions would adsorbed to the surface of as-prepared AgNPs, resulting in the aggregation of the adjacent AgNPs with the significant absorbance change (as shown in Scheme S1, Supporting Information). According to the Beer–Lambert law, there is a linear correlation between the MEL concentration and the absorbance of AgNPs. It can be used for rapidly and sensitively detecting MEL in milk sample in one step and the results were satisfactory. Additionally, for further improving the detection performance, the detailed mechanism underlying this special phenomenon was investigated.

Experimental

Chemicals and materials

All the reagents were of analytical reagent grade unless specified; distilled water was used throughout the experiments. All glassware used was cleaned in aqua regia ($HCl:HNO_3$, 3:1), rinsed thoroughly with triply distilled water, and oven dried prior to use.

MEL was purchased from Sigma (St. Louis, USA). Gallic acid (GA) was commercially purchased from Tianjin Yongda Reagent Development Center (Tianjin, China). Silver nitrate was supplied by Tianjin Kermel Chemical Reagent (Tianjin, China). Liquid milk and milk powder were purchased from local supermarket.

Instrumentation

The absorption spectra were recorded on a UV-1800 spectrophotometer (Shimadzu, Kyoto, Japan) with 1 cm path length cells. Fluorescence measurements were carried out at room temperature using a Hitachi 4600 spectrofluorimeter (Hitachi, Tokyo, Japan). An excitation wavelength (λ_{ex}) of 240 nm was used, and fluorescence intensities were recorded at 368 nm. Photographs for color changes were taken with a Panasonic DMC-FX 30 digital camera. A vortex mixer, MVS-1 (Jinbeide, Beijing, China), was employed to blend the solution.

All electrochemical experiments were performed with a CHI 650D electrochemical workstation (Chenhua, Shanghai, China). A bare glassy carbon disk electrode (2 mm in diameter) and a platinum wire (1 mm in diameter) were used as the working and counter electrodes, respectively. The reference electrode was a mercurous sulfate electrode (MSE) and all of the potential values are reported with respect to this electrode unless otherwise stated. A glassy carbon electrode was polished carefully to a mirrorlike surface with 0.3–0.05 μm of alumina aqueous slurry and then successively washed in an ultrasonic cleaner with water and ethanol.

The TEM sample was imaged using an H-7500 electron microscope (Hitachi, Japan) operating at 80 kV accelerating voltage at 200 k magnification. A typical sample for TEM was prepared by drying naturally a drop of solution containing silver nanoparticles at room temperature on a carbon-coated copper grid.

Colorimetric detection of MEL

The $[Ag(NH_3)_2]^+$ solution was prepared according to our previously published methods [39]: firstly, 95 mL of 1 mM $AgNO_3$ solutions were mixed with 3.8 mL of 10 mM NaOH, and then 3 mL of 0.25 M $NH_3{\cdot}H_2O$ solution were added into the mixture at room temperature. (*Caution! The solution is dangerous to form the explosive silver azide. It should be discarded quickly after using up.*)

Volumes of 2.5 mL of the as-prepared solution, and different concentrations of MEL were mixed in advance, and the mixture

was stirred thoroughly. Then a certain concentration of GA solution was added into the mixture. At last, the mixture was diluted to 5.0 mL with the triply distilled water, and blended thoroughly again. The absorption spectra data were collected 30 min later. It should be noted that the order of the addition of the reagents is very important and it could not be changed.

Extraction of real samples

Briefly, 1.8 g of milk powder was first mixed with 12 mL of 61 mM trichloroacetic acid and 4 mL of acetonitrile. After 15 min sonication and 15 min shaking, the mixture was centrifuged at 10,000 rpm/min for 15 min, and then the supernatant was filtrated twice through a 0.22 μm filter membrane to obtain the samples for detection. Because the milk from the supermarket is free of MEL, the as-prepared sample solution was spiked with certain amounts of MEL standard solution directly. The concentration of MEL was calculated by standard addition method. The liquid milk was also pretreated according to the above general procedure.

Results and discussion

Properties of MEL–AgNPs conjugate

Aggregation is accompanied with a simultaneous change in the absorbance of the AgNPs that can be observed in solution by UV–vis spectroscopy (Fig. S1A, SI) or visually (Fig. S1A insert). The remarkable color change from vivid yellow to pale red was found within 30 min upon the addition of MEL as shown in Fig. S1A. The color change of the formed AgNPs was also accompanied by the red-shift of the absorption peak to around 550 nm (Fig. S1A).

The test was performed in an assay format where MEL was added to the as-prepared $[Ag(NH_3)_2]^+$ solution. Following the GA added, the solution turn to pale red due to AgNPs came into close proximity with each other. It was documented that the MEL–AgNPs conjugates were formed. This is structure-specific and will not occur unless the target MEL is added. The interaction process of the as-prepared AgNPs with MEL can be visualized using TEM (see Figs. S1B and C). As shown in Fig. S1B, the as-prepared AgNPs were monodisperse in the absence of MEL. Strong aggregation of AgNPs was observed when MEL was added to the reaction solution of GA and $[Ag(NH_3)_2]^+$ (Fig. S1C).

Molecular linker-based aggregation mechanism

The aggregation of AgNPs in the presence of MEL induces a color change of solution, while no aggregation is expected for the other compounds. As we know, the oxidation capacity of Ag^+ is better than $[Ag(NH_3)_2]^+$ (cf. the curves *a* and *b* in Fig. S2, SI). We also collected a cyclic voltammogram of the GA in the presence of NaOH (curve *c* in Fig. S2) and compared it to that of the $[Ag(NH_3)_2]^+$ complex (curve *b*). The latter exhibited a smaller redox wave ($E_{1/2}$, which was the average of the oxidation and reduction peak potentials). Therefore, our results indicated that the reduction potential of GA in the basic is insufficient to reduce $[Ag(NH_3)_2]^+$ solution. Based on previous discussion [40], we supposed that the formed Ag_2O in the presence of a small amount of hydroxide ions is crucial in the $[Ag(NH_3)_2]^+$ reaction system.

Our strategy for designing the method for MEL is based on the interaction between MEL and Ag^+ of the adsorbed layer of the as-prepared AgNPs. It is well known that MEL, a triazine skeleton with three binding sites of nitrogen atom, can bind Ag^+ by means of coordination bond [41,42]. During the AgNPs formation process, the MEL molecule, which has been covalently bonded with the Ag^+, was adsorbed to the surface of as-prepared AgNPs, resulting in the aggregation of the adjacent AgNPs. So our sensing mechanism is based on the aggregation of AgNPs through the highly specific recognition of Ag^+ with MEL as given in Scheme S1.

To evaluate the mechanism described above, firstly, we intentionally used the others polyphenol compounds to conduct the same experiments, such as pyrogallol, and hydroquinone (see Fig. S3, SI). As can be seen, in the presence of MEL, other polyphenol compounds resulted in the similar changes in UV–vis absorption spectrum under the same experimental conditions. The only difference was the position and intensity of the UV–vis absorption peak of the formed AgNPs. The fact validated that the role of GA was only as reductant and stabilizing reagent. Therefore, it can be concluded that the addition of MEL does not form a new hydrogen bond with GA as a result of the reaction.

Then, in order to further confirm whether the MEL with Ag^+ can come into being the molecular interaction or not, the spectral and electrochemical properties of the system were investigated by UV–vis, fluorescence spectroscopy (Fig. S4, SI), and CHI electrochemical workstation (Fig. S5, SI). As shown in Fig. S4A, when a certain amount of MEL was mixed with $AgNO_3$, the UV–vis absorption peak of the solution was slightly shifted to longer wavelength compared to that of the single MEL or $AgNO_3$ solution. Again the fluorescence of MEL was quenched in the presence of $AgNO_3$ (see Fig. S4B). The trend was in good agreement with that observed in our UV–vis measurement. The electrochemical data were also recorded under the same conditions. The addition of MEL induces a shift of redox wave towards negative. These behaviors are attributed to the addition of MEL to produce an Ag–N covalent bond by a reaction.

Finally, intriguingly, the order of MEL addition, from another point of view, demonstrated the mechanism above is right. When MEL was added to the system before the GA, the color of the solution changed from yellow–green to brown quickly and evidently. However, if the sample addition sequence of MEL and GA is reverse, the color change is very slow and need about several hours. This evidence displayed that color reaction was thus ascribed to the interaction of the MEL and Ag^+ on the surface of colloids.

Selectivity of the developed strategy for the detection of MEL

Data related to the optimization process of MEL sensor are reported as SI (Fig. S6, SI). To further evaluate the selectivity of this method, the absorption intensity changes of the AgNPs upon addition of coexisting foreign inorganic ions and organic compounds in milk-including Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, glucose, lactose, sucrose, L-glutamic acid, L-cysteine, L-methionine, riboflavin, ascorbic acid, L-phenylalanine—were investigated under the same conditions separately. The A_{550nm}/A_{408nm} data were shown in Fig. S7 (SI). The AgNPs showed a remarkable quenching with only MEL molecules. As expected, most of the above-mentioned interferences showed a weak influence on the absorbance of the AgNPs although Fe^{3+} and ascorbic acid could interfere with the results a little. The interferences induced by Fe^{3+} and ascorbic acid may be attributed to the stronger redox capacity than do other foreign compounds. However, when the concentrations of these interferences were lowered to 0.5 μM, the quenching effects were weak. Thus, these interferences can be diminished by diluting the sample.

Calibration curves for quantification of trace MEL

The ratio of absorption intensity at 550 nm and 408 nm, A_{550nm}/A_{408nm}, was significantly increased at high concentrations of MEL which included the decrease of absorption at 408 nm and the increase of absorption at 550 nm (Fig. 1). According to the Beer–Lambert law, there is a linear correlation between the

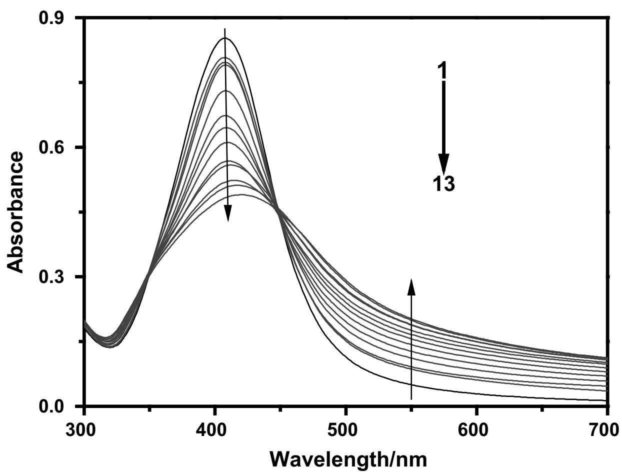

Fig. 1. Photographs (top) and UV–vis absorption spectra (bottom) of AgNPs in the presence of different concentrations of MEL: 0 nM (curve 1), 40 nM (curve 2), 80 nM (curve 3), 160 nM (curve 4), 240 nM (curve 5), 320 nM (curve 6), 400 nM (curve 7), 480 nM (curve 8), 560 nM (curve 9), 640 nM (curve 10), 720 nM (curve 11), 800 nM (curve 12), and 880 nM (curve 13).

concentration of MEL and the absorption ratio A_{550nm}/A_{408nm} of as-prepared AgNPs peak as shown in Fig. 2. The MEL could be quantified through 4×10^{-8} mol L^{-1} to 8.8×10^{-7} mol L^{-1}, and linear equation is $y = 0.0188 + 0.00513c$ ($R = 0.9991$, $n = 12$). The detection limit as signal to noise ratio of 3 was calculated to be 1×10^{-8} mol L^{-1}.

Detection of MEL in real samples

We detected MEL content in milk powder and dairy products. Following the pretreatment of real samples, a volume of samples was added to the $[Ag(NH_3)_2]^+$ solution according to the procedure

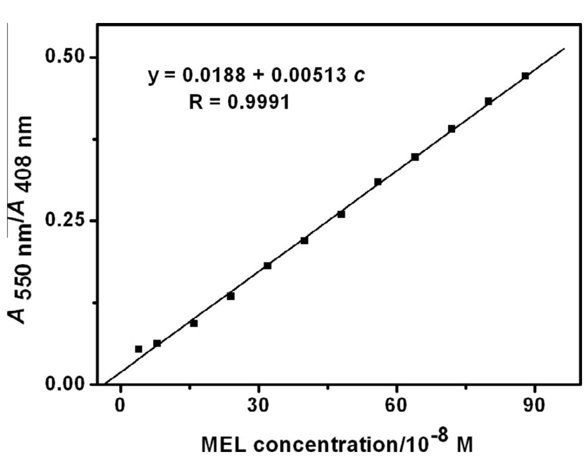

Fig. 2. The linear relationship between the A_{550nm}/A_{408nm} of AgNPs and the concentration of MEL over the range of 40–880 nM.

Table 1
Determination of MEL in milk samples by the standard addition method.

Samples	Added (nM)	Found[a] (nM)	Recovery[a] (%)	RSD[a] (%)
		ND[b]		
Milk powder	80	83	104	3.27
	240	234	97.5	2.98
	480	491	102	3.05
		ND		
Liquid milk	80	79	98.8	4.32
	240	251	105	4.83
	480	495	103	4.76

[a] All the values were the average of three measurements obtained.
[b] ND = not detected.

as described in the experimental section. The results are shown in Table 1. It was found that the method had a good recovery among 95–105%. It is demonstrated that the AgNPs can be applied to the real sample determination and this method is simple and convenient with no complicated requirement for instruments and reagents.

Conclusions

In conclusion, we have demonstrated a simple, quick and one-step assay method at room temperature for detecting MEL based on an in-situ formation of AgNPs through modified Tollens process. Detailed mechanistic investigations indicate that an Ag–N covalent bond between MEL and Ag^+ is critical for the aggregation of the forming AgNPs. The detection of MEL was realized during the formation of AgNPs, which was achieved in one step within 30 min. Our results show that as-prepared AgNPs can serve as a new prototype for illegal additives sensing systems in the dairy products, and it also has promising potentials for detection of various targets in optical chemosensors. It should be pointed out that our MEL sensor works in AgNPs solution, and sensing of MEL in the AgNPs solution has limited relevance. Sensing in AuNPs media that is more obvious in color change will be our further work in the near future.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.08.041.

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